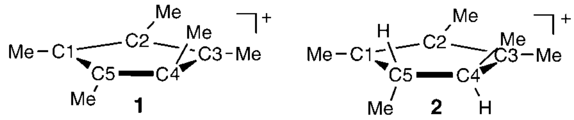
The Stable Pentamethylcyclopentadienyl Cation Remains Unknown**

Michael Otto, David Scheschkewitz, Tsuyoshi Kato, Mark M. Midland, Joseph B. Lambert, and Guy Bertrand*

For several years we have been interested by the stabilization of highly reactive species, such as silyl cations,[1] carbocations,[2a] carbenes,[2b] diradicals,[2c] and antiaromatic heterocycles;[2d] thus, cyclopentadienyl cations are of special interest for us. The parent compound ($C_5H_5^+$) is supposed to have antiaromatic character,[3] and the triplet ground state predicted from simple Hückel theory has been confirmed by ESR spectra[4] and by the latest ab initio calculations.[5] Like the $C_5H_5^+$ ion the pentamethylcyclopentadienyl cation ($C_5Me_5^+$) is predicted to have a triplet ground state, with the singlet state being 4.2 kcal mol^{-1} higher in energy.[5b] Jutzi and Mix[6] reported that the reaction of bromopentamethylcyclopentadiene with silver tetrafluoroborate or hexafluoroantimonate below $-30\,^{\circ}$C, led to a deep violet solution. In the ^{13}C NMR spectrum, only a broad signal attributed to the solvent was observable, which indicated the triplet nature of the cation. Polymers were formed upon warming this solution, but the pentamethylcyclopentadienyl cation has been trapped by various nucleophiles.

Based on this prior literature, the recent report on the isolation of the pentamethylcyclopentadienyl cation **1** by one of us[7] was therefore really fascinating and unexpected. The tetrakis(pentafluorophenyl)borate salt of **1** was described as a crystalline material, stable for weeks at room temperature, and that can be left open to the atmosphere without serious decomposition.

There were two major differences between the calculations and observations: the observed C4–C5 bond length (1.51 Å) was 11 % longer than the calculated one (1.36 Å), and in contrast to the calculated geometry, which predicted no pyramidalization of C4 and C5, their attached methyl groups protruded appreciably from the plane (CH_3-C4-C5-CH_3 dihedral angle = 106.9°; Figure 1). These differences were explained by crystal packing between the anion and the cation, which would pyramidalize C4 and C5, a distortion permitted by the weak π bonding. These would have been noncovalent nonbonded interactions. The resulting deformations would have been a trade off between coulombic attractions and nonbonded repulsions.

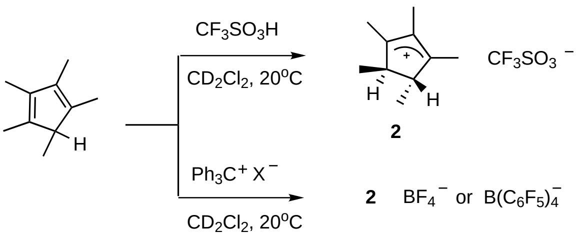


	1	2
^{13}C NMR (ppm)	C1 , C3 : 243 and 250	C1 , C3 : 244.5
	C2 : 153	C2 : 153.6
	C4 , C5 : 60	C4 , C5 : 60.6, JCH = 129,6
Bond lengths (Å)	C1-C2 : 1.41	C1-C2 : 1.40
	C2-C3 : 1.39	C2-C3 : 1.40
	C3-C4 : 1.48	C3-C4 : 1.49
	C4-C5 : 1.51	C4-C5 : 1.54
	C1-C5 : 1.50	C1-C5 : 1.50
Dihedral angle (°)	Me-C4-C5 -Me: 106.9	Me-C4-C5 -Me: 106.7

Figure 1. Comparison of ^{13}C NMR chemical shifts and geometric parameters for **1** and **2** (**1**: solid-state NMR spectroscopy and X-ray diffraction study; **2**: solution NMR and calculations).

Although reasonable these explanations were not totally convincing. Moreover, the observed dihedral angle between the methyl groups bonded to C4 and C5 and the C4–C5 bond length were in perfect agreement with a saturated fragment (C4–C5 single bond and the methyl groups in *trans* position). In other words, hydrogen atoms (difficult to observe by X-ray diffraction studies) might have been present on C4 and C5 and therefore the actual structure would be the already known[8] pentamethylcyclopentenyl cation **2**. This assumption was reinforced by the ^{13}C NMR chemical shift for the C4 and C5 carbons of **1** ($\delta = 60$), which are in the expected range for the corresponding sp^3 carbon atoms of **2** (Figure 1).[9]

To confirm our hypothesis, we first treated a CD_2Cl_2 solution of pentamethylcyclopentadiene with trifluoromethylsulfonic acid at room temperature (Scheme 1). According to ^{1}H and ^{13}C NMR spectroscopy, the protonation reaction was extremely clean. The ^{1}H NMR spectrum fits perfectly with that reported for compound **2**,[8b] while the ^{13}C{^{1}H} NMR spectrum ($\delta = 244.5, 153.6, 60.6, 23.6, 14.6, 10.8$ ppm) is also in good agreement with that reported for **1** (Figure 1).[7] Interestingly, the ^{13}C NMR proton-coupled spectrum indicates that the signal at 60.6 ppm arises from a CH carbon atom [^1J(CH) = 129.6 Hz]. Ab initio calculations (B3LYP/6-31G**)[10] were also carried out on compound **2** and the optimized geometry reproduces reasonably well the experimentally observed parameters for **1** (Figure 1).



Scheme 1.

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[*] Prof. G. Bertrand, M. Otto, Dr. D. Scheschkewitz, Dr. T. Kato, Prof. M. M. Midland
UCR-CNRS Joint Research Chemistry Laboratory, UMR 2282
Department of Chemistry
University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 909-787-4713
E-mail: gbertran@mail.ucr.edu

Prof. J. B. Lambert
Department of Chemistry
Northwestern University
Evanston, IL 60208-3113 (USA)

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We have checked that Cp*H (Cp* = C_5Me_5) reacts with triphenylmethyl tetrafluoroborate and tetrakis(pentafluorophenyl)borate salts to afford derivative **2** (< 50% yield; Scheme 1). This reaction is quite unexpected. Performing the previous experiments in deuterated solvents, or using Cp*D as a precursor, also leads to **2**, without deuterium atoms on C4 and C5. Therefore, we have to admit that the mechanism of this reaction is still obscure and requires further investigation.

In conclusion, there is no doubt that the reported pentamethylcyclopentadienyl cation **1**[7] is actually the pentamethylcyclopentenyl cation **2**. However, these recent developments will stimulate further research in this challenging area.

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Comment on the X-Ray Structure of Pentamethylcyclopentadienyl Cation

Thomas Müller*

In a recent communication Lambert and co-workers reported the unusual X-ray structure of singlet pentamethylcyclopentadienyl cation **1**.[1] Its molecular structure (**1a**, Figure 1) is highly localized with C1–C2 and C2–C3 distances expected for allyl cations (139.3 and 140.5 pm, respectively) and relatively long C1–C5 and C3–C4 bonds (148.2 and 150.0 pm, respectively). The most unusual and striking structural feature of this cation is, however, a very long formal C=C bond (151.0 pm) with strongly *trans* pyramidalized carbon atoms (dihedral angle $\Theta(H_3C\text{-}C4\text{-}C5\text{-}CH_3) = 107°$). It is noteworthy that the sum of the bond angles around the pyramidalized carbon atoms, C4 and C5, are 327.8° and 327.7°, very close to that expected for tetravalent carbon atoms.[2] Although the authors noted that this unusual geometry of the claimed cation **1** is not supported by theory,[1, 3] they attribute this distortion to crystal packing forces "permitted by the weak π bonding" between C4 and C5.[1]

Solid-state ^{13}C NMR spectroscopy of the crystalline material gives ^{13}C NMR chemical shifts for C1–C3 characteristic for allyl cations ($\delta = 250, 243$ (C1 and C3), 153 ppm (C2)).[1, 4] A resonance at $\delta\ ^{13}C = 60$ ppm was attributed to C4 and C5 (Table 1, entry 9),[1] a very unusual upfield shifted ^{13}C NMR signal for a formally sp^2-hybridized carbon atom.

The close structural and magnetic similarity of **1a** to allyl cations prompted us to reinvestigate the structure and NMR spectroscopy parameters of **1** and related allyl cations by

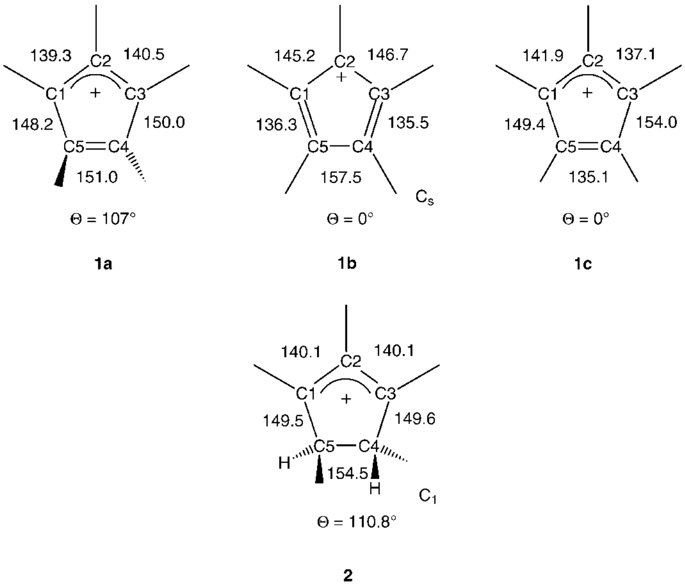

Figure 1. Experimental molecular structure of the cation **1a**[1] and calculated structures of singlet **1b** (B3LYP/6–31G(d)) and singlet **1c** (CASSCF(4/5)/6–31G(d)) and **2** (B3LYP/6–31G(d)); bond lengths [pm], dihedral angle Θ (Me-C4-C5-Me) [°].

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[*] Dr. T. Müller
Institut für Anorganische Chemie der Goethe Universität
Frankfurt/Main
Marie Curie Strasse 11
60439 Frankfurt
Fax: (+49) 69-798-29188
E-mail: Dr.Thomas.Mueller@chemie.uni-frankfurt.de

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